Aerobic oxidative desulfurization of model diesel using a B-type Anderson catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18} \cdot 3H_2O$

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ABSTRACT

A B-type Anderson polyoxomolybdates with mixed-valence molybdenum ions, $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo^{(V,VI)}_6O_{18}$, was prepared and characterized by Fourier transform infrared spectroscopy(FT-IR), UV–vis diffuse reflectance spectroscopy (UV–vis DRS), differential thermal analysis (DTA) and X-ray photoelectron spectrum (XPS). The polyoxometalate shows high catalytic activity in aerobic oxidative desulfurization of model diesel and the turnover number (TON) can reach about 4200 in absence of any sacrificial agent under mild conditions. The quaternary ammonium cations in the catalysts play a vital role in the aerobic oxidative desulfurization system. The catalytic activity for the oxidation of sulfur-containing compounds decreases in the order of 4,6-DMDBT > DBT > BT.

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1. Introduction

The deep removal of sulfur-containing compounds from fuel oils has attracted wide interests due to the stringent environmental regulations imposed on sulfur level in diesel [1–5]. Current technology of hydrodesulfurization (HDS) requires harsh conditions (e.g., high temperature, high pressure, and high hydrogen consumption), which result in high operating cost. Therefore, it is highly desired to develop non-HDS methods to produce clean diesel containing extremely low concentration of sulfur under mild conditions and also with low cost. Among ways that has been under investigation, oxidative desulfurization has received much attention because of its advantages of mild operating conditions and no consumption of H_2 [5–11]. Many types of oxidative systems have been attempted, using hydrogen peroxide and non-hydrogen peroxide compounds (e.g., t-butyl hydroperoxide, etc.) as oxidizing agent [6–12].

It has been expected that molecular oxygen or air instead of peroxides can be used as oxidizing agent under mild conditions for the oxidation of these refractory sulfur-containing compounds due to their characteristics of low price and green chemistry [13–18]. However, the presence of oxygen induced high activation barrier results in the huge difficulty in oxidative desulfurization of diesel under mild conditions. It has been proved [13–17] that the oxidation of these refractory compounds by molecular oxygen is only achieved at high temperatures or in the presence of a sacrificial

agent. Therefore, it is a challenge to seek an active catalyst for aerobic oxidative desulfurization under mild temperature and pressure.

Polyoxometalates (POMs) have attracted much attention in the fields of acid and oxidation catalysis, because their acidic and redox properties can be designed and tuned at molecular or atomic level. However, the Anderson-type POMs are not well known as catalysts [19,20]. Anderson-type heteropolyanions ($[YM_6O_{24}H_x]^{n-}$) possess a heteroatom (Y) in a central octahedral cavity of the crown by edge-sharing six octahedral MO_6 (M = Mo or W) [21]. These polyanions become a family for a number of 2+, 3+, 4+, 6+ and 7+ ions as the heteroatom. They are classified into types of A ($x=0$) and B ($x=6$) by the number of attached protons [22]. In our previous work [23], an A-type Anderson catalyst ($[(C_{18}H_{37})_2N(CH_3)_2]_5IMo_6O_{24}$) was reported, which can oxidize the sulfur-containing compounds in diesel under mild conditions to their corresponding sulfones using molecular oxygen as oxidant. We assumed that the other Anderson-type of polyoxomolybdates may also catalyze the oxidative desulfurization of diesel with similar reactivity, which led to further research into the type polyoxometalate in this study.

In this paper, aerobic oxidative desulfurization of diesel was developed, which was catalyzed by a B-type Anderson polyoxomolybdate with mixed-valence molybdenum ions ($[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$). The catalyst was proved to be effective in aerobic oxidative desulfurization with extremely high TON in absence of any sacrificial agent (Scheme 1). Our study provides an example of the mixed-valence molybdenum ions in the Anderson polyoxometalate and we particularly focus on the positive effect of mixed-valence of molybdenum ions in Anderson structure in the aerobic oxidative desulfurization.

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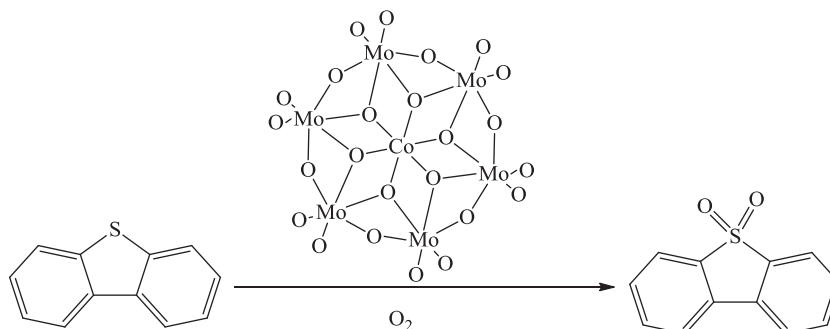
Scheme 1. Aerobic oxidation of DBT to the corresponding sulfone.

2. Experimental

2.1. Catalyst preparation

All the chemicals were of analytical grade and used as received. The Co (III) polyanion $(NH_4)_3Co(OH)_6Mo_6O_{18}$ was prepared according to the procedure reported in literature [22], a mixed aqueous solution ($30 cm^3$) of $CoSO_4 \cdot 7H_2O$ (0.015 mol) and 30% aqueous H_2O_2 (2 g) were added dropwise into the boiling aqueous solution of heptamolybdate (0.025 mol in $260 cm^3$ water). The obtained solution was refluxed for 10 min and then filtered while hot. The filtrate was set aside for crystallization.

$[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ was prepared as following: 10 mL ethanolic solution of quaternary ammonium (3 mmol) was added dropwise into a 40 mL aqueous solution of $(NH_4)_3H_6CoMo_6O_{24}$ (1 mmol) under stirring at room temperature. A light blue-green precipitate was immediately formed. After continuous stirring for 4 h, the resulted mixture was filtered and dried at 60 °C in vacuum for 24 h.

2.2. Characterization of catalysts

The infrared spectrum (IR) of the catalyst, diluted with KBr and pressed into a pellet, was recorded on a Nicolet 470 FTIR spectrometer. UV–vis diffuse reflectance spectroscopy (UV–vis DRS) was recorded on a TU-1901 (Beijing General Analytical Instrument Ltd Co., China) with $BaSO_4$ as the internal standard. The scanning patterns were recorded at 200–800 nm in a step-scan mode with a step of 5 nm. Differential thermal analyses (DTA) and thermogravimetric analyses (TGA) were carried out on NETZSCH STA409PC thermal analyzer with heating rate of $10 K min^{-1}$ from 298 to 873 K under nitrogen atmosphere. A cyclic voltammogram of 1 mM $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ was measured on a LK3200A instrument using a glassy-carbon as working electrode versus SCE. The measurement was carried out in a 0.1 M acetonitrile solution of $(C_4H_9)_4NBF_4$ with scan rate of $50 mV s^{-1}$. XPS spectrum was obtained by using Thermo ESCALAB 250Xi with Al Kα X-ray source. Pass energy was 20 eV and base pressure of analysis chamber was greater than 1×10^{-8} Pa. The spectra were calibrated against the reference binding energy of C 1s (284.8 eV).

2.3. Oxidation of model sulfur-containing compounds

In a typical experiment, the sulfur concentration was kept at 500 ppm by dissolving model sulfur-containing compound (BT, DBT or 4,6-DMDBT) in 25 mL Decalin. After this solution was heated to 80 °C and bubbled by molecular oxygen, catalyst was added. The solution in reaction was stirred vigorously and sampled periodically. The obtained samples were placed into an ice chamber for the termination of reaction and precipitation of most sulfones. The sulfur content in the upper clear solution was determined by microcoulometry after the catalyst and sulfones were precipitated by centrifugation.

3. Results and discussion

3.1. Characterization of the B-type Anderson catalyst

The IR spectrum of $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ is shown in Fig. 1. The spectrum of the catalyst reveals the characteristic bands of bridged Mo—O—Mo bonds in the molecule of hetropolyanione around 572, $653 cm^{-1}$, The bands at 890, 912 and $938 cm^{-1}$ are attributed to the terminal group of Mo=O bond and the band at $431 cm^{-1}$ is assigned to central Mo—O···Co modes [24,25]. In addition, the other peaks at 1470, 2852, 2922 and $3027 cm^{-1}$ belong to the vibrations of the quaternary ammonium cations.

UV–vis spectrum of $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ shows intense absorption in the range of 200–330 nm (Fig. 2), which is the characteristic of polymer Mo–O–Mo structures induced by charge transfer processes from O^{2-} to Mo^{6+} in octahedral coordination[24,26]. The two bands at 410 and 600 nm are the characteristic of Co^{3+} in the regular octahedral configuration, which are registered in the spectrum of cobalt heteropolymolybdate [24].

The weight loss was 2.1% around 160 °C in TG curves of $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ (Fig. 3). It suggests the molar ratio of water molecules to heteropolyanions is 3.1:1. The weight loss of 61.1% between 160 and 600 °C was resulted from the loss of quaternary ammonium cations. The total weight loss (63.2%) of the sample agrees with the calculated value of 64.7%.
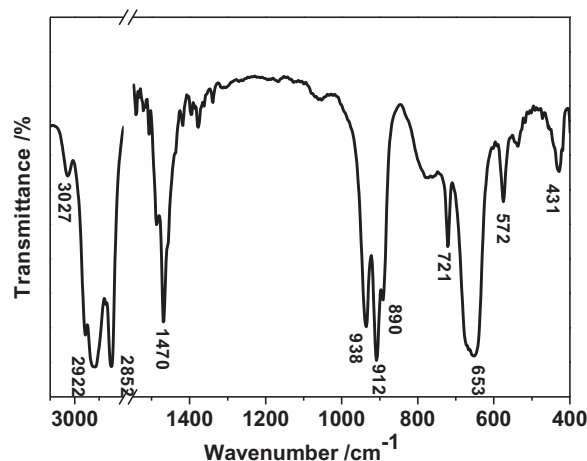

Fig. 1. The IR spectrum characterization of catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$.
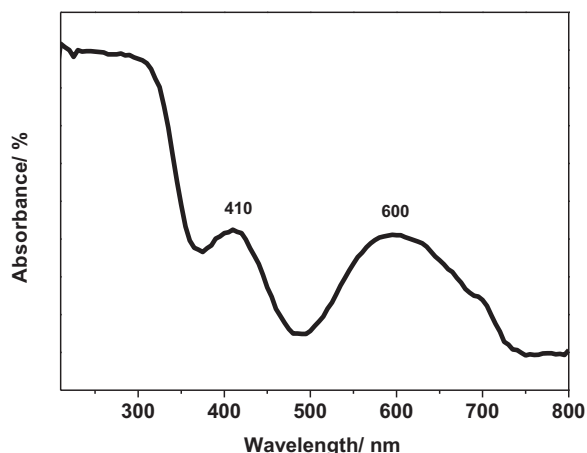
Fig. 2. The UV–vis DRS characterization of catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$.
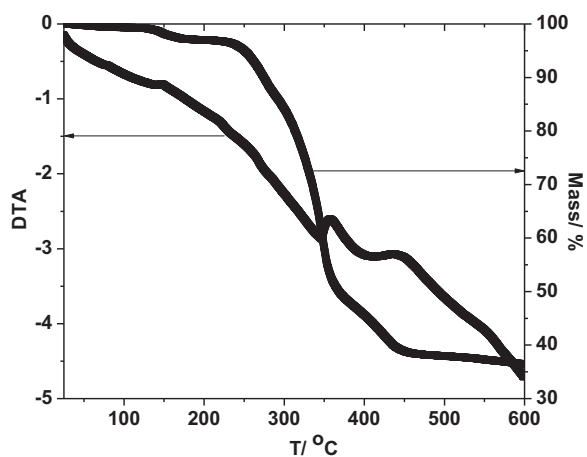

Fig. 3. The TG-DTA analysis of catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$.

These results indicate that the catalyst is mainly composed of $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}\cdot 3H_2O$.

In the potential range from 0.1 to 1.8 V vs SCE, cyclic voltammetry (CV) profile of $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ in 0.1 M acetonitrile solution of $(C_4H_9)_4NBF_4$ yielded an irreversible oxidation waves near $Epa = 1.36$ V vs SCE, which should be attributed to the irreversible redox steps of molybdenum (Fig. 4). CV curves of $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ in acetonitrile
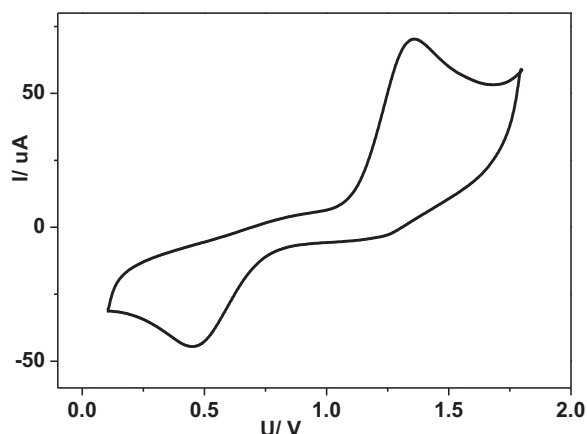

Fig. 4. The cyclic voltammogram of catalyst $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$.
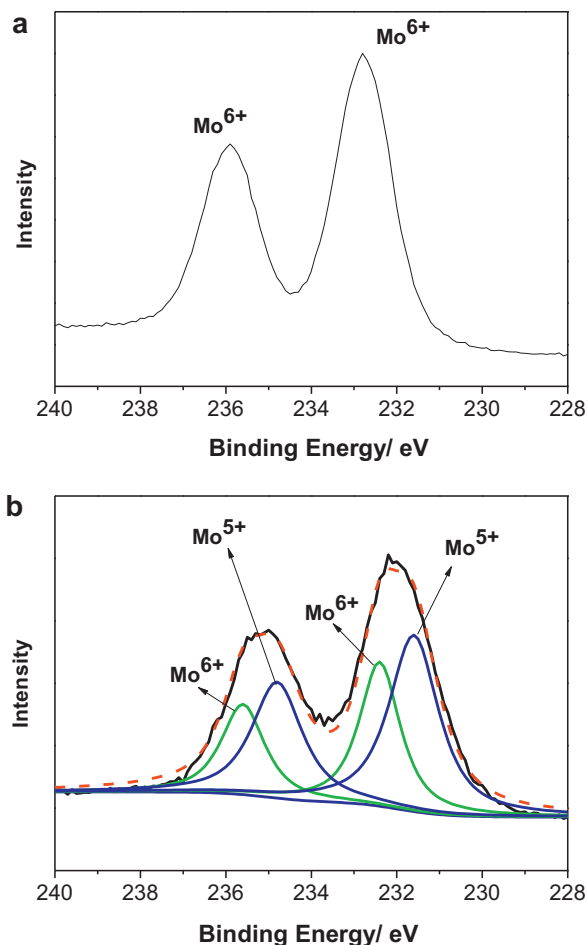

Fig. 5. XPS spectrum of the Mo 3d core level for $(NH_4)_3Co(OH)_6Mo_6O_{18}$ (a) and $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$. (b) The red dashed line is the fit of experimental data (black line) by Lorentzian–Gaussian peaks (blue and green lines). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

remains almost unchanged over 300 cycles at the scan rate of $50\,mV\,s^{-1}$, which indicates a good stability performance of this compound.

As shown in Fig. 5a, typical signal shapes of Mo 3d are observed on the XPS spectrum of $(NH_4)_3Co(OH)_6Mo_6O_{18}$, where the binding energy of Mo $3d_{5/2}$ (232.8 eV) is attributed to Mo^{6+} species. However in spectrum of $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ (Fig. 5b), mixed-valence of molybdenum can be found. The contribution of Lorentzian–Gaussian peaks centered at 231.6 eV is assigned to Mo^{5+}, while the small peaks centered at 232.6 eV are attributed to Mo^{6+}. These values agree with the reported values [27].

3.2. The aerobic oxidation of DBT using different catalytic system

Desulfurization of DBT in model diesel by different catalytic systems was investigated using molecular oxygen as an oxidant (Table 1). DBT in Decalin can be completely oxidized to corresponding sulfone at 80 °C in 7 h, however it cannot be oxidized in the absence of the catalyst in 12 h. It should be noted that DBT is hardly oxidized when $(NH_4)_3Co(OH)_6Mo_6O_{18}$ is used as a catalyst while the Anderson type catalysts with the quaternary ammonium cation can oxidize DBT to $DBTO_2$. Different catalytic performances of the two catalysts indicate that the quaternary ammonium cations in the catalysts play a vital role in the aerobic oxidative desulfurization [18,23]. The XPS studies (see Fig. 5a

Entry	Catalyst	Catalyst/S (molar ratios)	Reaction time (h)	Conversion of DBT (%)	TON
1	–	–	12	0	–
2	$(NH_4)_3Co(OH)_6Mo_6O_{18}$	1:100	12	5	5
3[b]	$Q_3Co(OH)_6Mo_6O_{18}$	1:100	7	100	100
4[b]	$Q_3Co(OH)_6Mo_6O_{18}$	1:50	7	100	50
5[b]	$Q_3Co(OH)_6Mo_6O_{18}$	1:500	10	100	500
6[b]	$Q_3Co(OH)_6Mo_6O_{18}$	1:1000	12	100	1000
7[b]	$Q_3Co(OH)_6Mo_6O_{18}$	1:10,000	12	42	4200

[a] Conversion of DBT was calculated as follows: {1-[(DBT concentration after reaction/DBT concentration before reaction)]}.
[b] Q: dioctadecyl dimethyl ammonium chloride (DODMAC).
Conditions: DBT (500 ppm) in 25 mL decalin, reaction temperature 80 °C and O_2 (1 atm).

and b) show that the valence of molybdenum ions in Anderson catalysts ($(NH_4)_3Co(OH)_6Mo_6O_{18}$) is +6, and the molybdenum ions in $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ present mixed-valence of +5 and +6. This result suggests that electrons are transferred from the electron-rich quaternary ammonium cations to Anderson structure, which reduces the high valence molybdenum ions to unstable and low valence ions. Intuitively, molybdenum can be easily oxidized from unstable low valence (+5) to high valence (+6) in oxygen atmosphere, leading to the activation of oxygen molecules. This result agrees with the conclusions in previous reports [28–30], which is that quaternary ammonium cation can activate molecular oxygen.

3.3. Effect of amount of catalyst on aerobic oxidation of DBT

To investigate the effect of catalyst amount on the oxidative properties, the oxidative desulfurization of DBT in model diesel was carried out at 80 °C in 1 atm dioxygen atmosphere with various amounts of catalyst (the mole ratio of $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ and sulfur is in the range of 1:50 to 1:10,000). As shown in Table 1 (entries 3–7), the Anderson polyoxometalate containing cobalt metal center ions presented excellent catalytic performance under mild condition for aerobic oxidation desulfurization. As the molar ratio of catalyst and DBT varied from 1:50 to 1:1000, 100% conversion of DBT could be obtained within 12 h (entries 3–6). It is noticed that the catalytic efficiency of the Anderson cobalt catalyst is extremely high and the TON can reach about 4200 (entry 7). To the best of our knowledge, this is the best performance of catalyst for aerobic oxidative desulfurization.

3.4. The ODS of different sulfur-containing compounds

Encouraged by the excellent performance of catalyst for the aerobic oxidation desulfurization, various sulfur-containing compounds were subjected to the reaction system at 80 °C in the presence of dioxygen for the test of Anderson cobalt catalyst. The results show that all the sulfur-containing compounds involved in this study can be oxidized to their corresponding sulfones. The catalytic activity for oxidation of sulfur-containing compounds decreases in the order of 4,6-DMDBT > DBT > BT (Fig. 6). It agrees with the results of our previous work [23], where it was reported that the reaction rate of these sulfur-containing compounds increases with the election density on sulfur atom. This reactivity trend reflects the intrinsic properties of the sulfur-containing compounds.

3.5. Possible mechanism of the aerobic oxidation of sulfur-containing compounds

The UV–vis spectra of catalyst in Decalin are significant different in presence or absence of molecular oxygen (Fig. 7). The
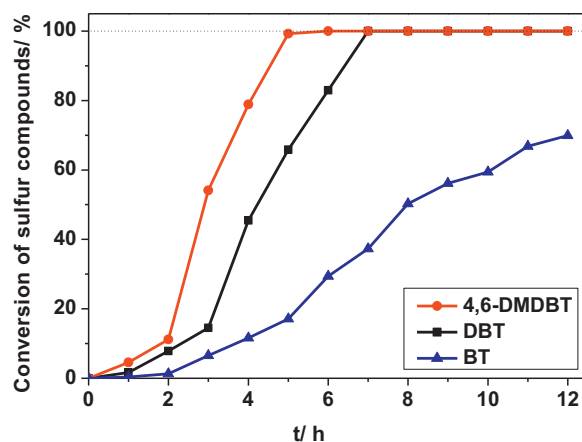

Fig. 6. The conversion of sulfur-containing compounds vs. reaction time at 80 °C. Conditions: $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$ (11 mg, 0.004 mmol), sulfur-containing compounds (500 ppm) in 25 mL Decalin, reaction temperature 80 °C and O_2 (1 atm).

absorption bands at 232 and 253 nm disappeared after 1 h dioxygen bubbling, which implied that this type Anderson catalyst reacted with dioxygen directly. This result does not agree with our previous work, probably owing to a different reaction mechanism [23]. Upon the addition of DBT, the characteristic peak of DBT at 237 nm was significantly decreased. This result suggested that DBT may be coordinated with the oxidized Anderson-type polyoxometalate.

Taking into account of XPS and UV–vis results, a mechanism is proposed as shown in Scheme 2. The Anderson-type polyoxometalate reacts with dioxygen leading to the oxidation of Mo^{5+} to Mo^{6+} and then the coordination of DBT with the oxidized Anderson-type polyoxometalate (that is a transition state). This activated DBT is
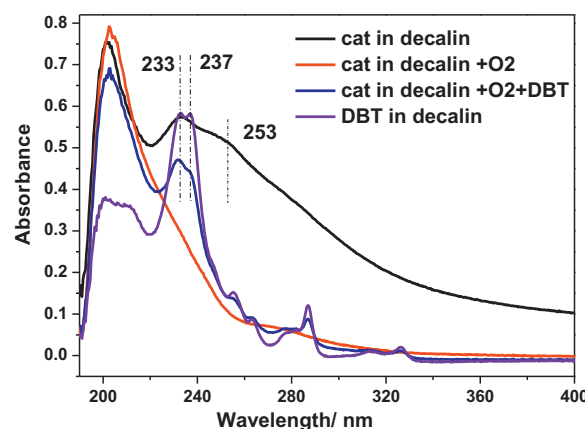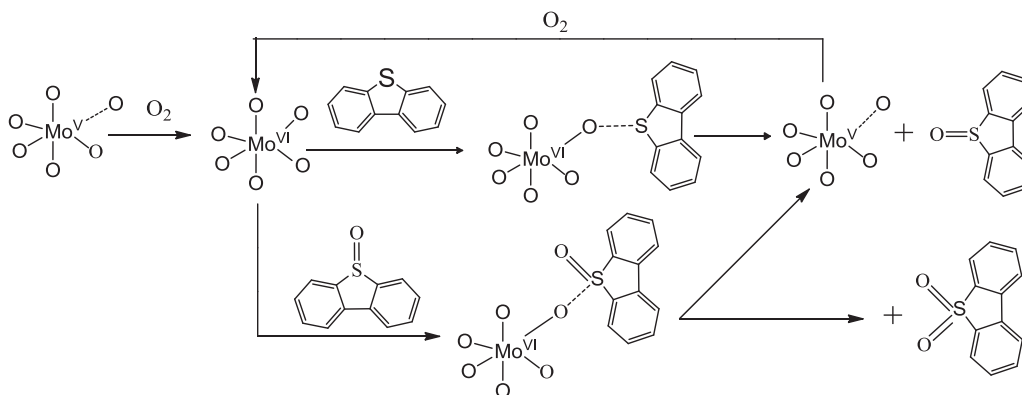

Fig. 7. UV–vis spectra of $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo_6O_{18}$. All spectra were collected from 0.01 mmol L^{-1} solutions.

Scheme 2. The proposed mechanism for dioxygen activation and aerobic ODS.

oxidized to the corresponding sulfone and the catalyst is reduced. The reduced catalyst is oxidized in presence of dioxygen to start another catalytic cycle.

4. Conclusion

In summary, Anderson type polyoxomolybdates with mixed-valence molybdenum ions, $[(C_{18}H_{37})_2N(CH_3)_2]_3Co(OH)_6Mo^{(V,VI)}_6O_{18}$, can aerobically oxidize sulfur-containing compounds in Decalin to corresponding sulfones in absence of any sacrificial agent under mild conditions. The high performance of this catalyst may be related to the mixed-valence of molybdenum ions in Anderson polyoxometalate. These results demonstrate that the aerobic oxidative desulfurization of diesel oils is a possible process for ultra-deep desulfurization.

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